BIOETHANOL PRODUCTION FROM CO-GASIFICATION OF LIGNOCELLULOSIC BIOMASS AND CHARCOAL

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Doctor of Philosophy

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis, and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy.

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Doctor of Philosophy

Faculty of Engineering Technology
UNIVERSITI MALAYSIA PAHANG

MAY 2019

ACKNOWLEDGEMENTS

Firstly, I would like to acknowledge my great debt of gratitude to all, who helped me over this research period. I would like to express my thanks to my main supervisor Dr. Azrina Binti Abd Aziz for all kind of mentoring, instructions and supported me enormously throughout my PhD studies. I would also like to thank my previous supervisors Dr. Abu Yousuf and Dr. Risky Ayu Kristanti for their cordial guidance. I wish to give a special thanks to the Prof. Madya Dr. Andri Kusbiantoro, Deputy Dean (Research & Postgraduates Studies), external examiners of Prof. Dr Suzana Binti Yusup and Prof. Dr. Hamidi Abdul Aziz, internal examiners of Prof. Madya Ts. Dr. Che Ku Mohammad Faizal Bin Che Ku Yahya, Dr. Samson Mekbib Atnaw and Dr. Nadzirah Mohd Mokhtar for their effective advice and comments during my PhD proposal defense, pre-viva and viva.

I would like to use this opportunity to express my sincere thanks to the Dean of Faculty of Engineering Technology (FTek), Prof. Dato' Ts. Dr. Zularisam Bin Ab Wahid for his cordial support throughout this work. I also extend my sincere thanks to the responsible persons in the Energy Management Laboratory, Toxicology Laboratory, Chemistry Laboratory and Cell Culture Laboratory for their kind cooperation with various instrumental facilities throughout my whole research. I would always appreciate the valuable support extended by all the academic and technical staff in the FTek. I would like to give cordial thanks to Prof. Dr. Md. Zahangir Alam, Faculty of Engineering, International Islamic University Malaysia (IIUM), Malaysia for providing me the microbial sample. I would also like to acknowledge the financial support of GRS Scholarship and PGRS (Internal Grant No. PGRS170370) received from University Malaysia Pahang, Malaysia.

I would like to acknowledge my university (Jashore University of Science and Technology, Jashore, Bangladesh) authority who provided me the permission for my study leave to start my PhD study at Universiti Malaysia Pahang (UMP). Afterward, I would like to convey my hearty thanks to the Dean of Institute of Postgraduate Studies, Prof. Dato’ Dr. Hasnah Binti Haron, and all other IPS staffs for their help throughout my study. I also owe my sincere appreciation to all the staff in the International Office (IO) for their timely help and support. Finally, I would like to thanks to my wife who inspired me all the time for the successful completion of my PhD. I would also like to extend my special appreciation to my heartiest parents, sister, nieces, brother-in-law, relatives, friends and colleagues for their cordial support.

ABSTRAK

Permintaan tenaga global kian meningkat disebabkan perindustrian dan perbandaran yang pesat. Oleh itu, peningkatan penggunaan bahan api fosil menjadikan permintaan tenaga global adalah kritikal. Bagi memenuhi permintaan tenaga, pendekatan alternatif adalah wajib. Kajian ini memberi penekanan mengenai pemeliharaan sumber tenaga boleh diperbaharui melalui lignoselulosik biomas (buah kelapa sawit, sisa hutan dan tempurung kelapa kosong) dan keluarannya (arang) untuk pengeluaran syngas dan bioethanol melalui proses hibrid thermokimia dan biokimia. Pencirian fizikokimia bahan bakar dilakukan untuk mengetahui potensi biotenaga mereka. Model simulasi dijalankan untuk mendapatkan keadaan optimum untuk penggabungan bersama berdasarkan beberapa tanggapan dengan menggunakan Aspen Plus® (V 8.6) di bawah keadaan operasi yang berubah (kadar aliran udara, kandungan lembapan dan komposisi bahan baku). Pelbagai campuran biomas dengan arang (0-40%) telah digabungkan bersama dalam gasifier downdraft (DG) untuk pengeluaran syngas. Faktor kawalan (iaitu, suhu, tekanan) reaktor dinilai pada pelbagai parameter iaitu nilai pemanasan, hasil syngas, kecekapan gas sejuk, kecekapan penukaran karbon, kecekapan exergy dan komposisi syngas untuk mengesahkan pengeluaran syngas semasa proses penggalian dengan udara (~35 m^3h^{-1}). Selepas itu, penapaian syngas dilakukan menggunakan bioreaktor TFB, dan pengeluaran bioethanol disiasat memandangkan pelbagai kesan (kekotoran syngas, suhu, pH, unit membentuk jajahan, jumlah karbon organik, komposisi syngas). Hasil awal syngas dicirikan oleh pengesan kekonduksian kromatografi gas dan hasil akhir bioethanol telah dikenalpasti oleh spektrometri massa-kromatografi Gas dan resonans magnetik nuklear (^{1}H). Analisis morfologi kajian ini mendedahkan bahawa dari segi pengegasan, lebih tinggi selulosa dan hemiselulosa yang mengandungi biomas lebih baik daripada arang. Variasi kepekatan reaktor downdraft menunjukkan kepekatan CO dan H_2 meningkat dengan meningkatnya arang (hingga 40%) dan peningkatan suhu (800-1000 °C) serta tekanan (25-35bar). Sebaliknya, trend yang bertentangan untuk kepekatan CO_2 telah diperhatikan dengan meningkatkan arang dalam reaktor. Walau bagaimanapun, kepekatan CH_4 relatif tidak berubah sepanjang tindak balas beberapa nisbah koefisien. Hasilnya, nisbah syngas optimum (H_2: CO) untuk tiga pengegasan bersama yang berbeza didapati 1.10-1.55 selepas biomas: campuran arang 70:30 dan 60:40 w/w untuk memaksimumkan faedah pengegasan proses. Secara berterusan, kepekatan pengeluaran bioethanol menggunakan yis (*Saccharomyces cerevisiae*) dan bakteria (*Clostridium butyricum*) masing-masing adalah 15.28 mmol/L dan 14.97 mmol/L. Oleh itu, biomas lignoselulosa yang terdapat di EFB, FR dan CS dengan arang oleh-produk boleh digunakan untuk penggabungan untuk pengeluaran syngas, dan seterusnya, ia juga sesuai untuk penukaran bioetanol melalui penapaian syngas menggunakan *Saccharomyces cerevisiae* dan *Clostridium butyricum*. Penyelidikan ini boleh menyumbang kepada syngas yang berpatutan dan mesra alam dan tenaga berasaskan bioethanol dan untuk mengurangkan kebergantungan kepada bahan api berasaskan fosil yang terhad.

ABSTRACT

Global energy demand is increasing due to rapid industrialization and urbanization. Moreover, augmented consumptions of fossil fuels make the global energy demand critical. So, to meet up the future energy demand an alternative approach is mandatory. The present study emphasizes on the valorization of mostly available renewable energy resources of lignocellulosic biomass (empty fruit bunch of palm oil, forest residue and coconut shell) and its by-product (charcoal) for the production of syngas and bioethanol through the hybrid process of thermo-chemical (co-gasification of feedstocks to syngas) and biochemical (microbial fermentation of syngas), respectively. The physiochemical characterization of feedstocks was performed to find out their bioenergy potentiality. The simulation model was carried out to obtain an optimum condition for co-gasification based on some assumptions using Aspen Plus® (V 8.6) under variable operating conditions (air flow rate, moisture content and composition of the feedstock). Then various mixtures of biomass with charcoal (0-40%) were co-gasified in a downdraft gasifier (DG) for syngas production. The controlling factors (i.e., temperature, pressure) of the reactor were evaluated on various parameters namely heating value, syngas yield, cold gas efficiency, carbon conversion efficiency, exergy efficiency and syngas composition to verify the production of syngas during the co-gasification process with air (~35 m^3h^{-1}). Subsequently, syngas fermentation was performed using a TFB bioreactor, and bioethanol production was investigated considering various effects (syngas impurity, temperature, pH, colony forming unit, total organic carbon, syngas composition). The initial yield of syngas was characterized by Gas chromatography-thermal conductivity detector and the ultimate yield of bioethanol was identified by Gas chromatography-mass spectrometry and Nuclear magnetic resonance (^1H) analysis. Morphological analysis of this study reveals that in terms of gasification, higher cellulose and hemicellulose containing biomass is better than the charcoal. The concentration variation of the downdraft reactor showed that the CO and H_2 concentration increase with the increasing charcoal (up to 40%) with increasing temperature (800-1000°C) and pressure (25-35bar). On the contrary, an opposite trend for the case CO_2 concentration was observed with increasing the charcoal in the reactor. However, CH_4 concentration was relatively unchanged throughout the reactions of several co-gasification ratios. Consequently, the optimal yield of syngas (H_2:CO) ratio for three different co-gasification was found to be 1.10-1.55 after the biomass:charcoal mixture of 70:30 and 60:40 w/w for maximizing the benefits of the gasification process. Successively, the concentration of bioethanol production using yeast (*Saccharomyces cerevisiae)* and bacteria (*Clostridium butyricum)* were 15.28 mmol/L and 14.97 mmol/L, respectively. Thus, the available lignocellulosic biomass of EFB, FR and CS with by-product charcoal could be suited for co-gasification for syngas production, and further, it is also suited for the conversion of bioethanol through syngas fermentation using *Saccharomyces cerevisiae* and *Clostridium butyricum*. This research may contribute to affordable and environment-friendly syngas and bioethanol-based energy and to reduce the dependency on limited fossil-based fuels.

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LIST OF SYMBOLS

°C	degree centigrade
g	gram
cm^{-1}	per centimetre
h	hour
L	litre
μm	micrometre
mg	milligram
ml	millilitre
mmol	millimole
mol	mole
mol L^{-1}	mole per litre
nm	nanometre
%	percentage
sec	second
cm^2	square of centimetre
mol%	mole percentage

LIST OF ABBREVIATIONS

EFB	Empty fruit bunch (of palm oil)
FR	Forest residue
CS	Coconut shell
MC	Moisture content
VM	Volatile matter
FC	Fixed carbon
AC	Ash content
S.C	*Saccharomyces Cerevisiae*
C.B	*Clostridium Butyricum*
TGA/DTG	Thermogravimetric and derivative thermogravimetry analysis
CHNS	Carbon, hydrogen, nitrogen and sulphur
FTIR	Fourier-transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometer
XRF	X-ray fluorescence
SEM-EDX	Scanning electron microscopy with energy dispersive x-ray spectroscopy
FESEM-EDX	Field emission scanning microscopy-energy dispersive x-ray analysis
TEM	Transmission electron microscopy
NMR	Nuclear magnetic resonance

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